Homogeneous Catalysis of High Free Fatty Acid Waste Cooking Oil to Fatty Acid Methyl Esters (Biodiesel)

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(Abstract) The waste cooking oil (WCO) is a promising feed stock for the production of biodiesel. The waste cooking oil used in this study has very high acid value (>13 mg KOH/g), therefore a simple base transesterification utilized so far proved to be unsuitable; this process resulted in soap formation. In this study the production process of fatty acid methyl esters (biodiesel) from WCO involved two steps, acid catalyzed followed by base catalysis reactions. In the first step, the acid value of WCO was reduced below 1 mg KOH/g by homogeneous acid catalysis and in the second step, acid catalyzed WCO was transformed to fatty acid methyl esters (FAME) in the presence of NaOH as homogeneous base catalyst. Five different sorts of FAMEs were identified in the waste cooking oil biodiesel by GC/MS analysis. The FAMEs recognized were methyl dodecanoate (C12:0), methyl tetradecanoate (C14:0), methyl hexadecanoate (C16:0), methyl 9-octadecenoate (C18:1) and methyl octadecanoate (C18:0). Their structures were confirmed by FTIR and NMR (^{1}H and ^{13}C) analyses. The percentage conversion of triglyceride to corresponding methyl esters determined by ^{1}H NMR was 97.89%. The biodiesel prepared was investigated for the fuel properties using ASTM standards.

Keywords: Waste Cooking Oil; High Acid Value; Homogenous Catalysis; Fatty Acid Methyl Esters; Fuel Properties.

1. INTRODUCTION

The alternative renewable fuels have gained immense attention due to the soaring price of petroleum products and depletion of fossil fuels. As a result, there is an earnest need to explore new energy sources, which should be economically competitive, technically viable and environmental friendly. Biodiesel is receiving great interest for future utilization all over the world because it is renewable in nature, environmental friendly and biodegradable [1]. Biodiesel is superior as compared to petroleum diesel in terms of flash point, amount of ash, and sulphur plus aromatic contents. The higher flash point of biodiesel makes it quite safe for storage and transportation. It is free from sulphur and aromatic compounds while petro diesel contain up to 500ppm sulphur content and 20-40 wt% aromatic compounds [2]. Accordingly, petro diesel is a huge source of black smoke particulate along with SO_2 emission and contributes to one third of the greenhouse gas emission by transport [3]. While, biodiesel has comparatively less discharge of CO, CO_2 and smoke density as compare to petro diesel [4].

The use of vegetable oil for biodiesel production has been extensively studies in recent years [5,6]. However, the high cost of vegetable oil and limited availability of feedstock are the critical issue for their use in the production of biodiesel. The biodiesel produced from vegetable oil has cost approximately 1.5 times greater than that of petro diesel [7], so the use of vegetable oil for biodiesel production is not feasible. Waste cooking oil (WCO) is a promising feedstock for the production of biodiesel. The cost of waste cooking oil is about 2-3 times less than that of virgin vegetable oil [7]. Large amount of waste cooking oil is available throughout the world. USA is producing 1.2-3 billion gallon of WCO per year whereas in Japan it is 4-6 lakh tons per year [8]. Production of biodiesel from this large amount of WCO also eradicates the environmental problems caused by the disposal of waste oil. WCO are, therefore, economical choice for the production of biodiesel. There are several methods for the formation of biodiesel such as, blending, micro emulsification, cracking and transesterification [9]. Among these methods transesterification is the simplest and efficient one.

In transesterification, the triglyceride molecules of the oil react with alcohol in the presence of catalyst to produce mono esters, called biodiesel. Generally, waste cooking oils contain a large percentage of free fatty acids (FFA) resulting in soap formation [10]. To avoid the soap formation new technologies should be employed. The pretreatment of the WCO with acid in the presence of alcohol will convert the FFA into esters as shown in **Figure 1(b)**.
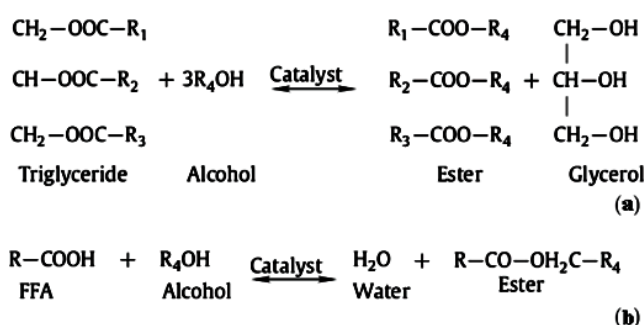
Figure 1 Chemical reaction of biodiesel production

Where R_1, R_2 and R_3 are the long alkyl chain of fatty acid and R_4 is the alkyl group of alcohol.

In this work, the WCO was first acid (H_2SO_4) catalyzed to reduce free fatty acid value and then base (NaOH) catalyzed using methanol (alcohol), to produce biodiesel. The fatty acid methyl ester (FAME) composition and fuel properties of WCO biodiesel were investigated. The fuel properties demonstrated the feasibility of WCO-based biodiesel to be used in diesel engines.

2. MATERIALS AND METHODS

2.1 Materials

The waste cooking oil used in this study was obtained from McDonalds' restaurant, Lahore, Pakistan. Analytical grade anhydrous methanol ($CH3OH$) of purity 99.8%, sodium hydroxide (NaOH), potassium hydroxide (KOH), sulfuric acid (H2SO4) and anhydrous sodium sulphate (Na2SO4) were obtained from Merck (Germany) and were used as such without further purification.

2.2 Experimental Setup

The apparatus used for the transesterification of WCO consisted of three neck round bottom flask equipped with reflux condenser and thermometer. The flask was placed on a heating plate equipped with the magnetic stirrer.

2.3 Homogenous Acid Catalysis

A specific amount of WCO was first filtered to remove the dirt and other solid food particles and then the acid value of the oil was determined by the method as described by the Maghraby [11], and found to be 13.33 mg KOH/g. The filtered WCO (100g) was poured in the reaction flask and temperature was increased to 65 oC. A solution of sulfuric acid in methanol was prepared by adding 2ml of H2SO4 into 30ml of methanol. The solution was added into the preheated WCO and stirred for 30 min. The resulting product was transferred to a separating funnel and allowed to be settled down. After few hours two layers were separated, the upper layer comprised of excess methanol, sulfuric acid while the other contained impurities. The lower layer was separated, washed with distilled water and dried with anhydrous sodium sulphate. The acid value measured

for the product was 0.4 mg KOH/g, thus it was used for further processing.

2.4 Homogenous Base Catalysis

The acid catalyzed oil was placed in the reaction flask and heated to the desired temperature (65oC). A solution of NaOH in methanol was prepared by adding 1g NaOH in 30 ml methanol. The freshly prepared solution was added into the pretreated oil and stirred at 65oC for 30 min. After the completion of reaction, the mixture was transferred to a separating funnel and allowed to separate in two layers. The upper layer contained biodiesel and was separated from lower glycerin layer. The biodiesel layer was washed three times with distilled water to remove soap and excess of NaOH. Finally the product was dried with anhydrous sodium sulphate and the yield was calculated by using the following equation [12].

$$\text{Yield (\%)} = (\text{Wt. of biodiesel}/\text{Wt. of oil}) \times 100 \qquad (1)$$

2.5 Biodiesel Characterization

The fuel properties of the biodiesel prepared from the waste cooking oil were determined using the ASTM standard methods. Kinematic viscosity (D 445), density (D 5002), cetane number (D 613), flash point (D 93), pour point (D 97), cloud point (D 2500), ash content (D 482), specific gravity (D 4052) and sulfur content (D 4294) were analyzed to evaluate the quality of the biodiesel prepared. The biodiesel prepared from waste cooking oil was analyzed by the FTIR using BRUKER VECTOR 22 spectrophotometer. The WCO biodiesel was analyzed by 1H NMR and 13C NMR using a Bruker AV 300MHz spectrometer. TMS and CDCl3 were used as internal standard and solvent respectively. 1H NMR spectrum was recorded with recycle delay of 1.0 s, pulse duration of 30o and 8 scans. 13C NMR spectrum was recorded with recycle delay of 1.89 s, pulse duration of 30o and 160 scans. The chemical composition of the prepared WCO biodiesel was characterized by the gas chromatography using GC-6890N model coupled with mass spectrometer; model MS-5973 MSD (mass selective detector). A DB-5MS capillary column of internal diameter of 0.32mm, length 30m, and film thickness of 0.25 m was used for separation of FAMEs. Helium was used as carrier gas at flow rate of 1.5 mL/min. The capillary column temperature was varied from 120 to 300 oC at a fixed rate of 10oC/min. A sample of volume 0.1 L waste cooking oil biodiesel in chloroform was injected using split mode with split ratio of 1:10. The mass spectrometer was set to scan from 50-550 m/z. Electron impact (EI) mode of ionization was used.

3. RESULTS AND DISCUSSION

The FAMEs (biodiesel) was synthesized from WCO using the two step process, acid (H2SO4) catalyzed followed by alkali (NaOH) catalyzed. The percentage yield of the

prepared biodiesel was calculated by using the Eq.1, which was about 94.8 %.

3.1. Fuel Properties of Biodiesel

The fuel properties of waste cooking oil biodiesel were investigated, which were measured by using ASTM standard methods. The results are summarized in Table 1 and compared with petro-diesel standards (ASTM D975). Results showed many advantages of waste cooking oil-based biodiesel over the petro diesel. The flash point of the fuel was measured for transportation, storage and safety consideration. Flash point of the biodiesel prepared (152oC) was within the biodiesel standard range but higher than petro diesel standard. This high value of flash point means biodiesel is less volatile which make it quit safer for transportation and storage. Ash contents showed the amount of metal present in the fuel. Metal particles deposited in the fuel system and internal engine parts and caused their abrasion. Thus, Prepared biodiesel possessed very less amount of ash contents than standard values, so engine would definitely remain clean. Another important property of fuel is kinematic viscosity, which controls the injector lubrication and fuel atomization. The viscosity of the prepared biodiesel is within the biodiesel standard range but slightly greater than petro diesel standard. This slight higher viscosity is used to provide lubrication to the moving parts of the engine. The WCO biodiesel is almost free from sulphur and the sulphur content was much less than the standard values. Consequently, the combustion of biodiesel would not produce sulphur oxide, hence, there would be no such problems associated with biodiesel, so the biodiesel production is environment friendly. Pour point and cloud point are the tests used to characterize the operation of fuel at low temperature. The biodiesel obtained has a higher value of pour and cloud points as compared to petro diesel standards but within biodiesel standard limits. The results showed that this biodiesel is suitable for moderate and high temperature climate. Cetane number is also a significant property of the fuel which is used to measure the combustion quality of the fuel. A higher cetane number leads to the shorter ignition delay, shorter duration of combustion and less occurrence of knocking.

Table 1 Fuel properties of waste cooking oil biodiesel

Fuel Property	ASTM method	Petro-diesel (D975)	Biodiesel standard (D6751)	WCO biodiesel
Flash point [oC]	D 93	60-80	100-170	152
Ash contents [wt %]	D 482	0.01	0.01	0.003
Kinematic viscosity [40oC, mm2/sec]	D 445	1.9-4.1	1.9-6.0	3.256
Sulphur contents [wt%]	D 4294	0.05	0.05	0.015
Cloud point [oC]	D 2500	-15 to 5	-3 to 12	10
Pour point [oC]	D 97	-35 to -15	-15 to 16	4
Cetane number	D 613	> 46	47 min	47.171
Density [40oC, g/cm3]	D 5002	0.834	0.86-0.90	863.64
Acid value [mg KOH/g]	D 664	0.50	0.80 max	0.471

The cetane number of prepared biodiesel was slightly greater than petro diesel standard, which showed that WCO biodiesel has excellent ignition and combustion properties. The density of waste cooking oil biodiesel was found to be 863.64 g/cm3 which was within the biodiesel standard limits. The acid value of waste cooking oil biodiesel was 0.471 mg KOH/g which was very less than the biodiesel standard value.

3.2. FTIR Analysis

FTIR spectroscopy was used as a fast and precise method for biodiesel analysis. As the biodiesel is mono alkyl ester so the characteristic peaks of esters in FTIR spectrum due to C=O and C-O bond around 1750-1730 cm-1 and 1300-1000 cm-1 respectively can clearly seen [13]. The other stretching vibrations of CH, CH2 and CH3 appear around 3050-3000, 2950-2850 and 2980-2950 cm-1 [14, 15].

The FTIR spectra of WCO and its biodiesel were very similar but some differences were also present. The band position of the carbonyl group changed due to substituent groups. The ester carbonyl group in the biodiesel showed a different absorption band of C=O vibration than ester carbonyl group in the oil. The peak of this band changed from 1742.6 in oil to 1741.4 in biodiesel. Change in the position of some other groups was also observed from 1463.3, 1376.8 and 1159.7 in oil to 1456.4, 1365.3 and 1166.2 cm-1 in biodiesel. Some new peaks appeared in the biodiesel at 1435.6, 1228.8, 1216.7, 1203.8 and 881.3 cm-1 indicate the conversion of oil into biodiesel.

3.3. NMR Analysis

The WCO biodiesel was characterized by the 1H and 13C NMR. The 1H NMR spectrum of the waste cooking oil biodiesel is shown in Figure 2. To evaluate the conversion of oil into biodiesel, a new signal appeared at 3.606 ppm. This signal indicated the formation of biodiesel, because the peak well matched the range of proton from the methyl ester group (COOCH3). To evaluate the conversion of methyl ester, we used ⁻CH2 protons at 2.24 ppm. These two peaks confirmed the conversion of oil into biodiesel. Other observed peaks were at 0.828 ppm due to terminal methyl protons, a strong signal at 1.214 ppm from the methylene proton of carbon chain, a signal at 1.569 ppm related to ⁻carbonyl methylene proton and at signal at 5.28ppm associated to olefinic proton. Eq.2 described the conversion of triglycerides into methyl esters [12, 16].

$$C = (2A_{Me}/3A_{CH_2}) \times 100 \qquad (2)$$

Where C is percentage conversion of triglyceride to corresponding methyl esters, AMe is integration value of the methoxy protons of the methyl esters and ACH2 is integration value of the ⁻CH2 protons. The percentage conversion of triglyceride to corresponding methyl esters by using Eq.2 was found to be 97.89%.
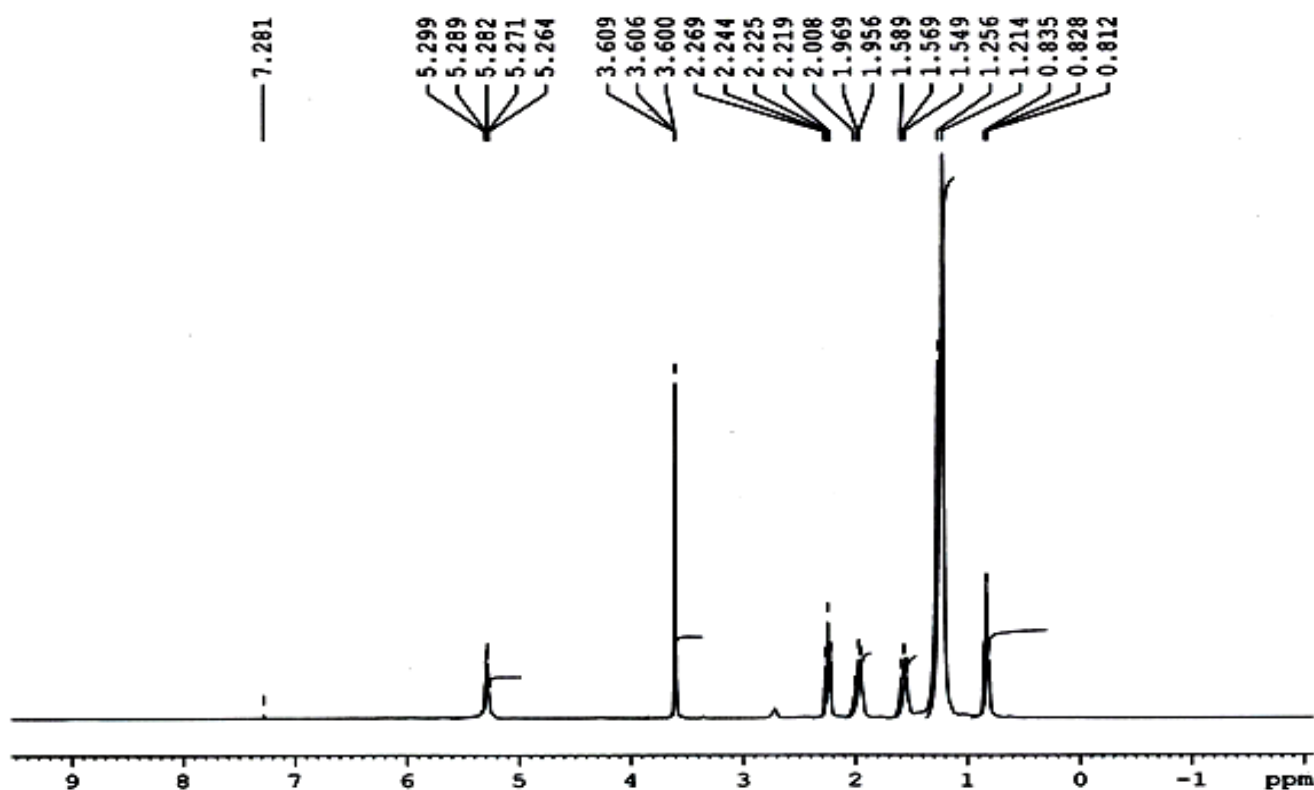
Figure 2 ^{1}H NMR of waste cooking oil biodiesel
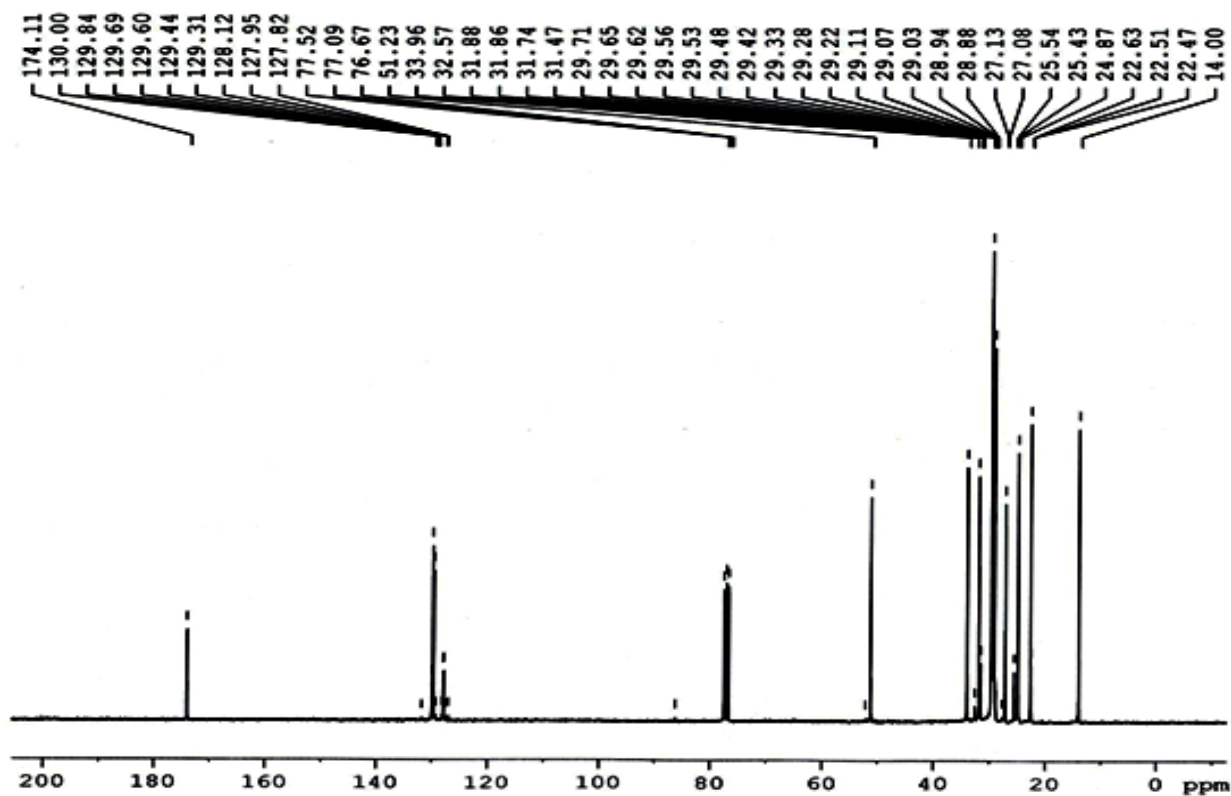
Figure 3 ^{13}C NMR of waste cooking oil biodiesel

Compared with literature values [2, 17] biodiesel prepared by this method had greater conversion of triglycerides into methyl esters.

The 13C NMR spectrum of the waste cooking oil biodiesel is shown in Figure 3. The characteristic peak of the ester carbonyl carbon (COŌ) was observed at 174.11ppm and that of CO carbon was found at 51.23ppm. Two peaks at 127.82 and 129.60 ppm indicated the unsaturation in the fatty acid methyl esters. A signal at 14.00 ppm was due to the terminal methyl carbon. Other observed peaks from 22.47 to 33.96 ppm were related to the methylene carbons of carbon chain of methyl esters.

3.4. GC/MS Analysis

The GC/MS study was performed to determine the fatty acid methyl ester composition of the waste cooking oil biodiesel. The gas chromatogram of the waste cooking oil biodiesel is shown in Figure 4. In the gas chromatogram five peaks were observed and each peak corresponds to a fatty acid methyl ester. These fatty acid methyl esters were identified by the library match software (NO. NIST 02). The identified fatty acid methyl esters were confirmed by mass spectrometric analysis and are shown in Table 2.

The four saturated fatty acid methyl esters identified in the waste cooking oil biodiesel have characteristic fragmentation pattern. In the mass spectra of all these saturated fatty acid methyl esters, the base peak was observed at m/z 74 which was due to the McLafferty rearrangement process. Two other peaks, one at [M̄31]+ due to loss of methoxy group and other at [M̄43]+ due to Table 2 Fatty acid methyl esters composition of waste cooking oil biodiesel

Table2 Fatty acid methyl esters composition of waste cooking oil biodiesel

Identified compound	R. t. (min)	Formula	Corresponding Acid
Methyl dodecanoate	6.561	C13H26O2	C12:0
Methyl tetradecanoate	8.810	C15H30O2	C14:0
Methyl hexadecanoate	11.049	C17H34O2	C16:0
Methyl 9-octadecenoate	12.972	C19H36O2	C18:1
Methyl octadecanoate	13.065	C19H38O2	C18:0

rearrangement of chain and hydrogen atom, followed by loss of propyl radical, were also detected in the mass spectra of all saturated fatty acid methyl esters. Other distinct ion peak appeared at m/z 87 due to ¯ cleavage [CH3OOC(CH2)2]+ and series of peaks observed at m/z 87, 101, 115, 129, 143,........., due to cleavage of [CH3OOC(CH2)n]+, where n=2, 3, 4, 5, 6,.........., with a difference of 14 a.m.u. Thus ¯ cleavage and alkyl series supported the identification of saturated fatty acid methyl esters. Figure 5 shows the mass spectrum of methyl dodecanoate. One monounsaturated fatty acid methyl esters were identified which have characteristic fragmentation pattern. The base peak of these fatty acid methyl esters was observed at m/z 55 due to the loss of butenyl group. Two other characteristic peaks were also appeared, one at [M̄32]+ due to loss of methoxy and one hydrogen and the second at [M̄74]+ due to loss of McLafferty ion. These three distinct peaks were used for the identification of monounsaturated fatty acid methyl esters. Other characteristic ions include hydrocarbon ions [CnH2n-1]+, [CnH2n]+, and [M̄88]+, [M̄102]+, [M̄116]+ etc. due to the loss of a fragment containing the carbonyl group by cleavage between carbon (3,4), (4,5) and (5,6) with addition of rearranged hydrogen atom.
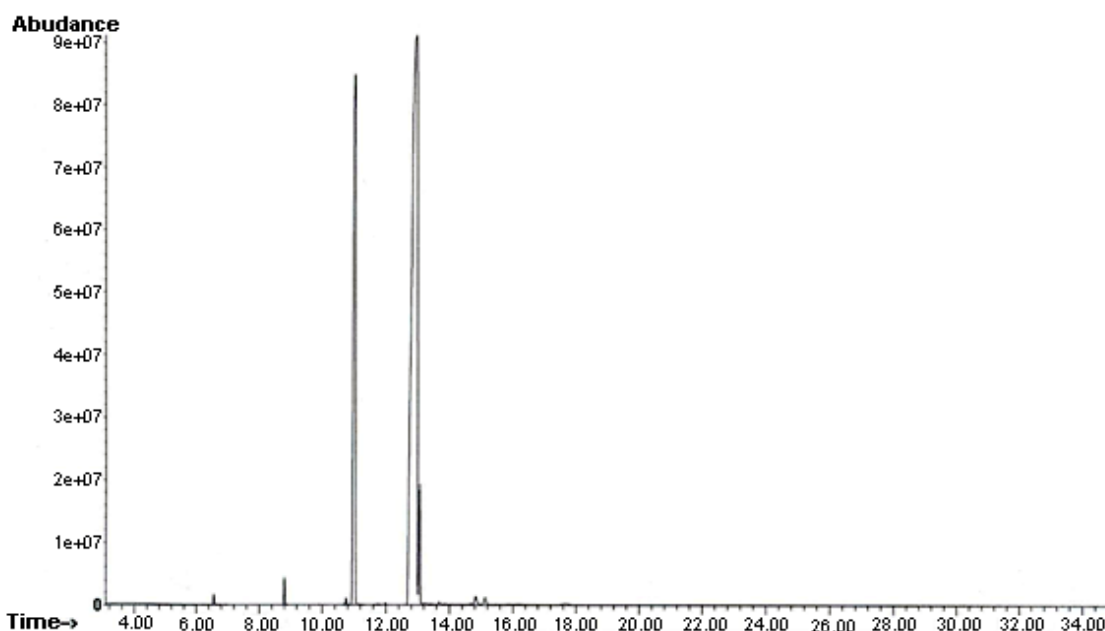

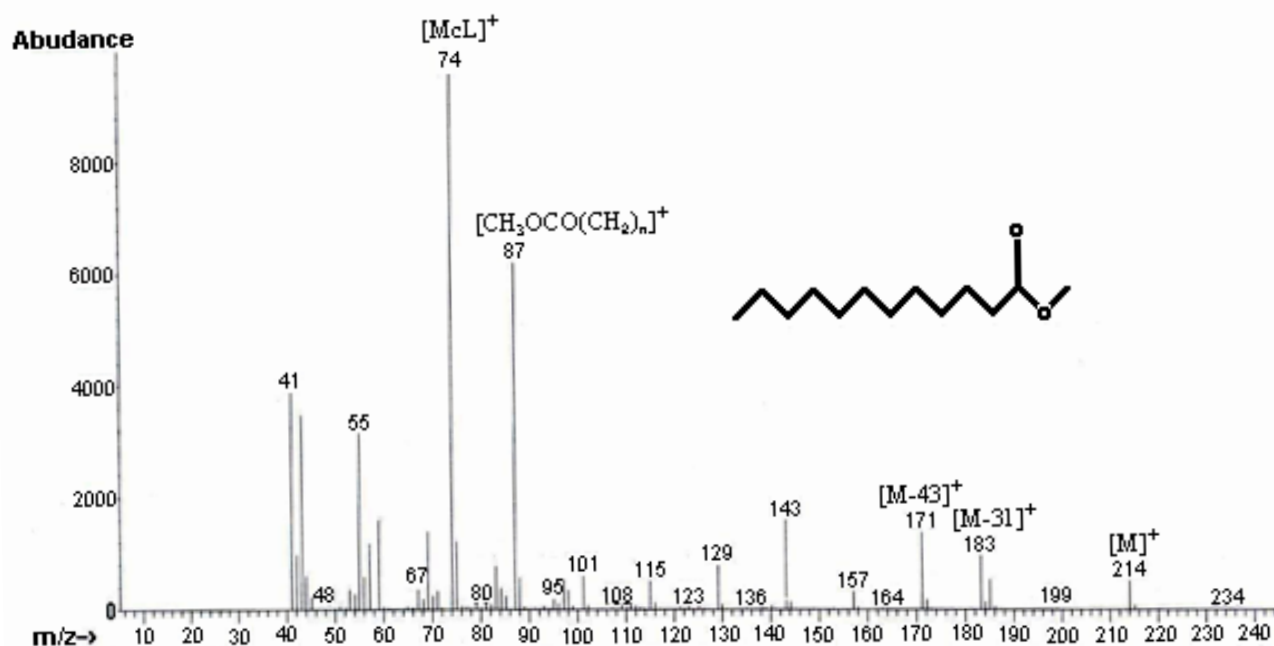**Figure 4** The gas chromatogram of waste cooking oil biodiesel

Figure 5 Mass spectrum of methyl dodecanoate from waste cooking oil biodiesel

CONCLUSIONS

Fatty acid methyl esters of waste cooking oil were successfully synthesized by two-step homogenous catalysis. The method employed was proved to be an excellent method for the conversion of high free fatty acid value oil to biodiesel. The synthesis of biodiesel was confirmed by the FTIR, NMR analyses. The chemical composition of methyl esters was determined by using GC/Ms analysis. Five fatty acid methyl esters were identified in waste cooking oil biodiesel from C12 to C18 by chromatographic retention time data and verified by mass fragmentation pattern. The fuel properties of the prepared biodiesel were investigated and compared with ASTM petro diesel and ASTM biodiesel standards. The determined density, viscosity, flash point, sulphur content, cetane index, acid value, cloud point, pour point and ash content were well within the ASTM standard limits. Flash point, ash and sulphur contents showed the advantage of waste cooking oil biodiesel over the petro diesel. Hence, the waste cooking oil biodiesel is an excellent substitute of petro diesel.

4.ACKNOWLEDGEMENTS

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